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ANALYTICAL STUDY OF THE WORK FUNCTION CHARACTERISTICS OF A METAL IMMERSED IN CESIUM VAPOR - SURFACE CONTRIBUTION

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TECHNICAL PREPRINT prepared for Twenty-Fourth Annual Conference on Physical Electronics sponsored by Massachusetts Institute of Technology Cambridge, Massachusetts, March 25-27, 1964

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION · WASHINGTON, D.C. · 1964

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It is well known that adsorbed cesium significantly reduces the electron work function of the emitter and collector in a cesium thermionic diode. Figure 1, which is based on the data reported by Houston[1] of General Electric, shows how this reduction in electron work function $-\Delta\varphi_e$ varies with the ratio of metal surface temperature to cesium reservoir temperature T_S/T_{Cs}. (All symbols are defined in the appendix.)

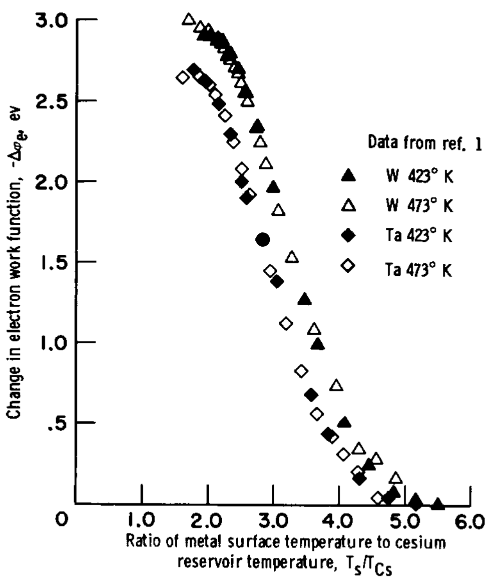

Figure 1. - Work function variation as function of ratio of surface to cesium temperature.

In an effort to derive an analytic expression to represent data of the type shown in figure 1, it is found that the metal surface plays a far more important role in the adsorption process than that attributed to it in the literature. It will be shown that because of the presence of the metal surface it is necessary to consider the effective electric field acting on each adsorbed particle, the effective polarizability of each adsorbed particle, and a new expression for the variation in atom desorption energy with gas coverage.

Consider the model of an adsorbed particle shown in figure 2. Let $\vec{E}_{eff,i}$ be the effective dipole field acting on the i^{th} adsorbed particle. Because of this field, the effective dipole moment $\vec{m}_{eff,i}$ of this particle is changed by $2\alpha_i\vec{E}_{eff,i}$ to yield a new effective dipole moment $\vec{p}_{eff,i}$ given by the relation

$$\vec{p}_{eff,i} = \vec{m}_{eff,i} + 2\alpha_i\vec{E}_{eff,i} \tag{1}$$

The effective dipole field $\vec{E}_{eff,i}$ consists of the field $\vec{E}_{ii}$ produced by the image of the dipole $\alpha_i\vec{E}_{eff,i}$ induced in the i^{th} adsorbed particle by $\vec{E}_{eff,i}$ and the field $\sum_{\substack{k=1\\k\neq 1}}^{\infty} \vec{E}_{ik}$ produced by all the other effective dipoles (adsorbed particles); that is,

$$\vec{E}_{eff,i} = \vec{E}_{ii} + \sum_{\substack{k=1\\k\neq 1}}^{\infty} \vec{E}_{ik} \tag{2}$$

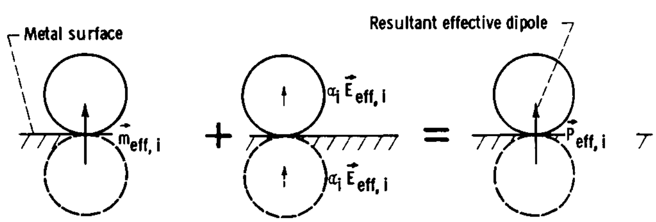

Figure 2. - Model illustrating change in effective dipole moment of adsorbed particles in presence of other adsorbed particles.

Assuming that the field $\vec{E}_{ik}$ acting on the ith adsorbed particle is uniform and equal to $\vec{E}_{ik}$ at the surface yields

$$\vec{E}_{ii} = 2\,\frac{\alpha_i\vec{E}_{eff,i}}{z_{o,i}^3} \tag{3}$$

$$\vec{E}_{ik} = -\frac{\vec{p}_{eff,k}}{r_{ik}^3} \tag{4}$$

Substituting equations (3) and (4) into equation (2) leads to the important new result

$$\vec{E}_{eff,i} = -\frac{1}{1 - \frac{2\alpha_i}{z_{o,i}^3}} \sum_{\substack{k=1 \\ k\neq 1}}^{\infty} \frac{\vec{p}_{eff,k}}{r_{ik}^3} \tag{5}$$

Using the previous expression for $\vec{E}_{eff,i}$ in equation (1) yields the following equation for $\vec{p}_{eff,i}$:

$$\vec{p}_{eff,i} = \vec{m}_{eff,i} - \frac{2\alpha_1}{1 - \frac{2\alpha_i}{z_{o,i}^3}} \sum_{\substack{k=1 \\ k\neq 1}}^{\infty} \frac{\vec{p}_{eff,k}}{r_{ik}^3} \tag{6}$$

If the configuration of the effective dipoles associated with the adsorbed particles is assumed to be a Topping square array, equation (6) may be written as

$$\vec{p}_{eff} = \frac{\vec{m}_{eff}}{1 + 9.033\ \alpha_{eff}(N_s\theta)^{3/2}} \tag{7}$$

where all dipoles are considered identical, and the effective polarizability α_{eff} is defined as

$$\alpha_{eff} = \frac{2\alpha}{1 - \frac{2\alpha}{z_o^3}} \tag{8}$$

It should be noted that the new and unique feature in equation (7) is the use of the effective polarizability α_{eff} in the denominator. For the cesium tungsten system, analysis of Taylor and Langmuir's data[2] yields the value of 18.7 $\mathring{A}^3$ for the effective polarizability α_{eff} of adsorbed cesium.

The atom desorption energy φ_a is the work $W_{s-\infty}$ needed to take an adsorbed particle from the surface to infinity in the form of an atom. Thus, it may be written as

$$\varphi_a = W_{s-\infty} \tag{9}$$

or

$$\begin{aligned}\Delta\varphi_a &= \Delta W_{s-\infty} = -\Delta W_{\infty-s} \\ &= -\left[\frac{1}{2}\alpha\left|\vec{E}_{eff}\right|^2 - \frac{\vec{p}_{eff}}{2}\cdot\vec{E}_{eff}\right]\end{aligned} \tag{10}$$

The first term within the bracket in equation (10) is the polarization energy, the second is the interaction energy of the adsorbed particles and the effective dipole field acting on them where $\vec{E}_{eff}$ is the effective dipole field given by equation (5). In terms of $|\vec{m}_{eff}|$, $\vec{p}_{eff}$, α_{eff}, and z_o, equation (10) becomes

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$$\Delta\varphi_a = -\frac{1}{4\alpha_{eff}}\left(1 + \frac{\alpha_{eff}}{z_o^3}\right)\left(|\vec{m}_{eff}|^2 - |\vec{p}_{eff}|^2\right) \tag{11}$$

Since

$$\Delta\varphi_e = -2\pi e N_s(\vec{p}_{eff} \cdot \hat{n})\theta \tag{12}$$

and

$$\vec{p}_{eff} \cdot \hat{n} = \pm|\vec{p}_{eff}| \tag{13}$$

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equation (11) may be written in the form

$$\Delta\varphi_a = -\frac{1}{4\alpha_{eff}}\left(1 + \frac{\alpha_{eff}}{z_o^3}\right)\left[|\vec{m}_{eff}|^2 - \frac{1}{4\pi^2 e^2 N_s^2}\left(\frac{\Delta\varphi_e}{\theta}\right)^2\right] \tag{14}$$

The previous expression is the desired equation for the atom desorption energy.

Equation (14) is compared to the data of Taylor and Langmuir[2] on the variation in cesium atom desorption energy from a tungsten surface. The values for $|\vec{m}_{eff}|$ and α_{eff} are determined from their work function data, and z_o is chosen so that the calculated values of $-\Delta\varphi_a$ fit the data at medium and at high coverages. The various values used are

$$\left.\begin{aligned} |\vec{m}_{eff}| &= 9.70 \text{ Debyes} \\ \alpha_{eff} &= 18.7 \text{ Å}^3 \\ z_o &= 3.22 \text{ Å} \\ N_s &= 4.8\times10^{14}/\text{cm}^2 \end{aligned}\right\} \tag{15}$$

Figure 3 shows the comparison of the calculated and experimental values of $-\Delta\varphi_a$. Points for the solid line are computed from equation (14), and points for the dotted line are computed from

$$\Delta\varphi_a = \frac{1}{4\alpha_{eff}}\left[|\vec{m}_{eff}|^2 - \frac{1}{4\pi^2 e^2 N_s^2}\left(\frac{\Delta\varphi_e}{\theta}\right)^2\right] \tag{16}$$

which is equation (14) with the term α_{eff}/z_o^3 set equal to zero. Equation (16) corresponds to the case in which an adsorbed particle's own image field is not taken into account in the determination of the total dipole field acting on it.

It is interesting to note that the polarizability α of adsorbed cesium computed from equation (8) with the values of α_{eff} and z_o given in equation (15) is 6.00 Å^3, which is quite close to the ionic polarizability of cesium. Also, the value of $z_o/2$ is close to the ionic radius of cesium.

In this paper it has been shown that the correct polarizability that should be

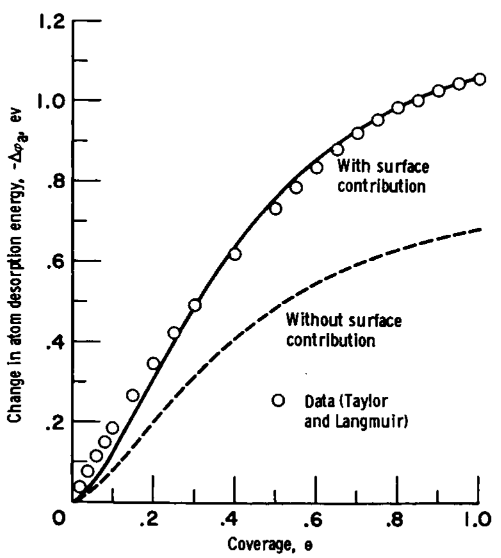

Figure 3. - Variation in cesium atom desorption energy from tungsten surface as function of cesium coverage.

used in equation (7) is the effective polarizability defined by equation (8). In addition, it is demonstrated that the variation in atom desorption energy is closely related to the variation in electron work function with coverage.

APPENDIX - SYMBOLS

e	electronic charge
$\vec{E}$	dipole field
$\vec{E}_{eff}$	effective dipole field
$\vec{m}_{eff}$	effective dipole moment as coverage approaches zero
$\hat{n}$	unit vector normal to and coming out of surface
N_s	number of adsorption sites per unit area
$\vec{p}_{eff}$	effective dipole moment at coverages greater than zero
r_{ik}	distance between i^{th} and h^{th} adsorbed particles
T_{Cs}	cesium reservoir temperature
T_s	surface temperature
$W_{s-\infty}$	work required to take a particle from surface to infinity
$\Delta W_{s-\infty}$	change in work required to take a particle from surface to infinity
$\Delta W_{\infty-s}$	change in work required to take a particle from infinity to surface
z_o	distance between center of an adsorbed particle and center of its image
α	polarizability of an adsorbed particle
α_{eff}	effective polarizability of an adsorbed particle
θ	coverage, or fraction of surface occupied by adsorbed particles
φ_a	atom desorption energy
$\Delta\varphi_a$	change in atom desorption energy
$\Delta\varphi_e$	change in electron work function

Subscripts:

i,k	i^{th} and k^{th} adsorbed particles

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2. Taylor, John Bradshaw, and Langmuir, Irving: The Evaporation of Atoms, Ions and Electrons from Caesium Films on Tungsten. Phys. Rev., vol. 44, no. 6, Sept. 15, 1933, pp. 423-458.